^{13}C N.M.R. DIPOLAR DEPHASING AS A PROBE INTO THE STRUCTURE OF AUSTRALIAN OIL SHALE KEROGENS AND PYROLYSIS RESIDUES

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ABSTRACT

The solid state nuclear magnetic resonance (n.m.r.) technique of dipolar dephasing was applied to a range of Australian oil shale kerogens and pyrolysis residues of an aliphatic shale (Rundle, Queensland), in order to gain more information on chemical structure than can be obtained from a conventional cross polarization spectrum. From these measurements the proportion of aliphatic carbon that is methyl or non-protonated in an aromatic shale and the pyrolysis residues was estimated. Non-protonated carbon was found to be unimportant and thus it was shown that the methyl content varied according to shale type and/or thermal history. The proportion of aliphatic methyl carbon in residues, generated at a range of temperatures from 400-500°C, was found to increase with increasing reaction temperature. This trend indicates that the β-bond in alkyl chains attached to aromatic ring structures is cleaved in preference to the α-bond during shale pyrolysis.

INTRODUCTION

Dipolar dephasing ^{13}C n.m.r has been extensively employed in determining the fraction of aromatic carbon that is protonated in a range of solid samples including model compounds, coals and other geochemical materials [1-17]. In many heterogeneous samples the decay of aromatic signal intensity with increasing carbon magnetization holding time (t_1) can be expressed, in terms of the decay constants T'_{2A} and T'_{2B}, as the sum of two exponential decays from protonated and non-protonated aromatic carbon, respectively. A separation of the aromatic signal intensity into two components is possible as the minimum T'_{2B} values for model aromatic ring compounds are five times the T'_{2A} values obtained for methine carbon [1]. However, this was not found to be the case for oil shales [18]. We have attributed this difference in relaxation behaviour to the intrinsic nature of the oil shale kerogen. Either the non-protonated carbons are in close proximity to protonated structures and thus have reduced T'_2 values, which approach those of the protonated carbons, and/or there are significantly more protonated carbons present, which still dominate the total signal intensity at $t_1 \geqslant 45$ μs, when only signal from non-protonated carbon is normally observed.

Little work has been undertaken to investigate the chemical structure of the aliphatic components of fossil fuels by n.m.r. Some studies have been reported on coals [1], but data on oil shales are not currently available. Thus, in this work we have examined the potential of dipolar dephasing as a probe of the chemical structure of the aliphatic components in Australian shales and shale pyrolysis residues. The fraction of aliphatic carbon that is methyl in the most aromatic shale and the pyrolysis residues has been estimated. This is related to kerogen structure and the mechanism of shale pyrolysis.

THEORY

The technique of dipolar dephasing is based on the rapid loss of signal intensity from protonated carbons, when a time period (t_1), in which the proton decoupler is turned off, is inserted before data acquisition in a conventional cross polarization program. The rate at which signal intensity is lost is dependent on the magnitude of the carbon-hydrogen dipolar interaction. Hence carbons bonded to protons experience stronger dipolar interactions than non-protonated carbons, unless the dipolar interaction is modulated by molecular motion, e.g. rapid rotation of

methyl groups. It has been shown for some compounds (19) that at a dipolar dephasing time of 50 μs the signal intensity from methine and methylene carbons is almost completely eliminated from the conventional cross polarization spectrum. Resonances from quaternary carbons remain, although attenuated in intensity due to long range, weak interactions with protons. Methyl carbon resonances also remain if the methyl groups present are free to rotate at speeds sufficient to severely weaken the carbon-proton interaction. This is possible in almost all solids including coals (1).

For carbons that are weakly coupled to protons, model compound studies have shown that the decay of signal intensity is simply exponential with increasing dipolar dephasing time (t_1) (5,7,20). However, for strongly coupled methylene and methine carbons, signal intensity decays as a function of time squared, i.e. a Gaussian decay pattern (5,7,20). In more complex systems such as coals the decay of aliphatic signal intensity is closer to exponential than Gaussian, however similar T_2' values are normally obtained from either Gaussian or exponential calculations (1).

For kerogen residues and highly aromatic shales (aromaticity (f_a) > 0.60), which contain methine, methylene, quaternary and methyl carbons, our results (Figure 1) show that the decay of aliphatic signal intensity can be described as the sum of two decays given by Equation 1.

$$I_T = I_s^o \exp-[t_1^2/2T_2'(S)^2] + I_w^o \exp-[t_1/T_2'(W)]$$ 1)

where I_T is the total aliphatic signal intensity; I_s^o is the initial signal intensity of the strongly coupled aliphatic carbons (CH_2,CH); I_w^o is the initial signal intensity of the weakly coupled aliphatic carbons (C,CH_3); t_1 is the delay period where the decoupler is gated off; and $T_2'(S)$ and $T_2'(W)$ are respectively the decay constants for the decay processes of strongly and weakly coupled carbon types.

If one approximates that the signal intensity of the strongly coupled carbons has decayed to a negligible amount after a delay period of 50 μs, then Equation 1 simplifies to

$$I_T = I_w^o \exp-[t_1/T_2'(W)]$$ 2)

I_w^o can therefore be determined from the zero time extrapolated intercept of the graphed data for t_1 > 50 μs (see Figure 1). $T_2'(W)$ is obtained from the reciprocal slope of the least-squares fit to the data. These parameters can then be used to obtain data on the decay of the strongly coupled carbons. The plot of ln [$I_T - I_w^o \exp-t_1/T_2'(W)$] versus the square of t_1 (1) yields a linear relationship and $T_2'(S)$ is obtained from the slope.

The parameter, $f_w(Ali) = I_w^o/(I_w^o + I_s^o) = I_w^o/I_T^o$, gives the fraction of aliphatic carbon that is methyl or non-protonated. $F_w(Ali)$ is related to the fraction of total carbon that is methyl or non-protonated (f_w), by (1-f_a), where f_a is the fraction of total carbon that is aromatic, i.e.

$$f_w = f_w(Ali) \times (1-f_a)$$ 3)

Alternatively, when only a single exponential decay is observed (Figure 2), an estimate of $f_w(Ali)$ can be made indirectly from the signal intensity of the aliphatic resonance at $t_1 = 0$ μs and a delay time at which all methylene and methine carbon has decayed completely (1). A delay of 50 μs would be appropriate for the oil shale samples examined. However, as the T_2' values of the aliphatic kerogens are > 25 μs, indicating that the methine and methylene groups in the kerogens are highly mobile, this approach is not applicable to oil shales.

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EXPERIMENTAL

Sample Preparation

All samples were demineralized by hydrochloric/hydrofluoric acid treatment (18) prior to analysis by n.m.r.

Pyrolysis residues of Rundle shale (Queensland, Australia) were generated from pyrolysis experiments using a modification of the Fischer Assay method (ASTM D3904-80). Shale, crushed to -100 mesh, was heated to various temperatures between 400-500°C at a rate of 12.5°C/min, and held isothermally at temperature for the time specified between 10-40 min. The raw shale used in these experiments contained 13.35% organic C, 2.3% H, 1.3% S, 0.4 % N and 1.25% inorganic C on a dry weight basis. The major inorganic components were clay minerals (illite, kaolinite and montmorillonite), quartz, siderite, calcite and pyrite.

N.M.R.

Solid-state ^{13}C n.m.r. spectroscopic measurements were made on a Bruker CXP 100 instrument at 22.6 MHz. Kerogen was packed in a boron nitride rotor with a Kel-F base. The dipolar dephasing program chosen for this study used alternate phase inversion of the 90° r.f pulse to minimize baseline artifacts, and a refocusing 180° pulse along the spin locking co-ordinate was inserted in the middle of the t_1 period to avoid linear phase distortions. The 90° pulse width was 4.5-8 μs, with a recycle time of 0.8-1 s. Data were collected in 1 K of memory, zero filled to 4 K and Fourier transformed using line broadening factors of 30-100 Hz. Dipolar dephasing delays (t_1) between 2-200 μs were used and each experiment continued until 4,000-6,000 scans were acquired. Results were calculated from integrated signal intensities divided at the point of inflection between 80-100 ppm.

RESULTS AND DISCUSSION

Results obtained from dipolar dephasing experiments of a selection of Australian kerogens, with a range of aromatic carbon contents (f_a) are presented in Table 1. Figure 2 shows a typical plot of the logarithm of aliphatic signal intensity versus t_1 for a kerogen of low aromaticity (f_a = 0.21). Only an average T_2' value (T_{2C}') can be determined for the decay process. A slowly decaying component with a $T_2^{2C} > 30$ μs is not apparent in the plot; this indicates a very low concentration of methyl carbon in the kerogen. Figure 1 shows a similar plot for a highly aromatic kerogen (f_a = 0.60). The decay process is clearly not exponential and two rate constants governing the decay, $T_2'(S)$ and $T_2'(W)$, can be determined respectively from Gaussian (Figure 3) and exponential data calculations using Equations 1 or 2. Since two decay processes can be observed for the Condor carbonaceous shale and only one for the aliphatic shales then the aliphatic structures of the Condor carbonaceous kerogen contain large concentrations of methyl and/or non-protonated carbon whereas kerogens of lower aromatic content have relatively much lower concentrations of these species. The aliphatic moieties of the Glen Davis, Rundle, Condor brown and Nagoorin kerogens must consist mainly of chain methylene and methine carbons and an insignificant amount of quaternary carbon, whereas the highly aromatic kerogen must contain aromatic ring structures associated with relatively short alkyl chains and aliphatic cross-linking structures.

The T_{2C}' data calculated from dipolar dephasing experiments of shale pyrolysis residues from the Rundle deposit (Queensland) are listed in Table 2. The T_{2C}' values for the residues are greater than those of the aliphatic kerogens. However, the loss of aliphatic signal intensity is more appropriately described as a sum of two decays. The decay constants for strongly coupled carbon, $T_2'(S)$, lie near the lower limit for the time constants quoted for methylene and methine carbons (12-29 μs)

TABLE 1
DIPOLAR DEPHASING DATA FOR THE ALIPHATIC COMPONENTS
OF AUSTRALIAN OIL SHALES[a]

Kerogen	f_a	Atomic H/C	T'_{2C} (μs)	$T'_2(S)$ (μs)	$T'_2(W)$ (μs)	$f_w(Ali)$	f_w
Glen Davis	0.19	1.52	29	-	-	-	-
Rundle	0.21	1.55	26	-	-	-	-
Condor brown	0.25	1.41	26	-	-	-	-
Nagoorin	0.49	0.83	28	-	-	-	-
Condor carbonaceous	0.60	0.93	55[b]	16[c]	88[c]	0.45	0.18

[a] T'_{2C} values are the average T'_2 values determined from exponential fit to all t_1 data points.

[b] Values obtained when data fitted to single exponential decay.
[c] Values obtained using Equation 1.

TABLE 2
DIPOLAR DEPHASING DECAY DATA FOR THE ALIPHATIC COMPONENTS OF SHALE
PYROLYSIS RESIDUES FROM THE RUNDLE DEPOSIT (QUEENSLAND)[a]

Pyrolysis conditions Temperature (°C)	Time (min)	f_a	Atomic H/C	T'_{2C} (μs)	$T'_2(S)$ (μs)	$T'_2(W)$ (μs)	$f_w(Ali)$	f_w
425	10	0.33	1.26	46	19	67	0.69	0.46
425	20	0.52	1.17	52	20	82	0.64	0.31
400	40	0.38	1.18	48	16	69	0.58	0.36
425	40	0.64	1.01	57	-[b]	76	0.78	0.28
450	40	0.81	0.74	52	-	-	-	
475	40	0.85	0.64	65	-	-	-	

[a] T'_{2C} values determined from exponential fit to all t_1 data points.
[b] Insufficient points for accurate determination.

(20). The decay constants for weakly coupled carbons, $T_2'(W)$, are all less than 100 µs suggesting a predominantly methyl contribution to the signal intensity. Hence the $f_w(Ali)$ estimates obtained for the residues reflect an increase in the proportion of aliphatic carbon that is methyl with increasing pyrolysis temperature.

The decay of aliphatic signal intensity from the highly aromatic residues could not be resolved into two components for a number of reasons. The aliphatic content of these residues is low, and there is a small contribution from spinning side bands to the total aliphatic signal intensity, owing to the greater chemical shift anisotropy of these samples. At $t_1 > 45$ µs these contribute most of the signal intensity in the aliphatic region and the small 'real' aliphatic signal becomes buried. Nevertheless chemical shift data (Figure 4) show that there is an upfield shift of the centre of the aliphatic resonance with increasing pyrolysis temperature of the shale residues. This resonance, centred at 31 ppm in the raw kerogen, approaches a value of 16 ppm, similar to the chemical shift expected for methyl carbon, in the high temperature residues. This progressive increase in methyl carbon content of the shale residues is more clearly illustrated by dipolar dephasing experiments. Figure 5 shows the spectra obtained after a dipolar dephasing delay of 2, 30 and 60 µs from Rundle shale and a low (425°C) and high (475°C) temperature pyrolysis residue. The aliphatic peak of the raw shale is narrow, sharp and unsplit after a delay time of 60 µs. In the 425°C residue set, a shoulder emerges from the central aliphatic resonance after a 30 µs delay and a distinct separation of a methyl resonance is obvious after a 60 µs delay. A marked upfield shift of the whole aliphatic resonance occurs after a 30 µs delay in the high temperature residue. Thus our results indicate that the proportion of aliphatic carbon that is methyl increases significantly with increasing pyrolysis temperature.

These results allow some conclusions to be drawn about the mechanism of shale pyrolysis. Although the fraction of total carbon that is methyl or non-protonated in the residues (f_w) appears to decrease with increasing pyrolysis temperature (Table 2), the aliphatic carbon of the pyrolysis residues contains a larger proportion of methyl groups than the parent shale (Rundle). Thus alkyl chains in the kerogen must be preferentially cleaved β to aromatic rings rather than α to aromatic rings during pyrolysis. It is noteworthy that similar behaviour has been observed in residues from the flash pyrolysis of coals (21).

CONCLUSIONS

Dipolar dephasing studies on shales and shale residues can yield useful information about the structure of the aliphatic components present in these solids. It has been demonstrated that in an Australian shale (Condor carbonaceous) with a high aromatic carbon content ($f_a = 0.60$) the aliphatic carbon consists of a high proportion of methyl groups whereas shales of lower aromaticity (Glen Davis, $f_a = 0.19$; Rundle, $f_a = 0.21$; Condor brown, $f_a = 0.25$ and Nagoorin, $f_a = 0.49$) all have very low methyl contents.

The dipolar dephasing behaviour of the aliphatic signal of the Condor carbonaceous shale can be resolved into a rapidly decaying component, with a signal intensity dependent on the square of the dipolar dephasing time and a slower exponentially decaying component. Similar behaviour has also been observed for pyrolysis residues from a highly aliphatic shale (Rundle). These results together with chemical shift data show that when shale is pyrolysed the proportion of aliphatic carbon that is methyl increases with increasing pyrolysis temperature up to 500°C. Hence during pyrolysis the β-carbon-carbon bond of alkyl chains attached to aromatic rings is cleaved in preference to the α-bond, i.e. methyl groups are more stable.

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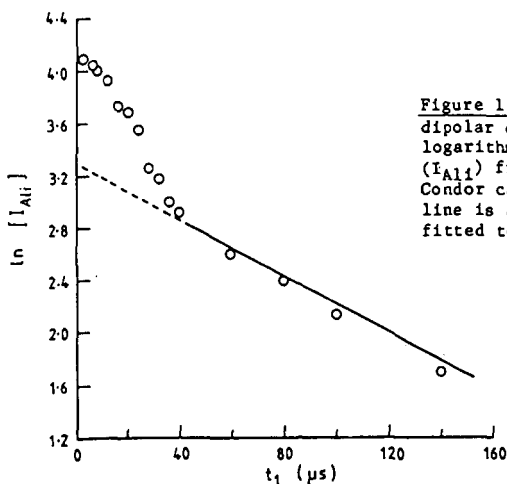21. P.J. Collin, R.J. Tyler and M.A. Wilson. Fuel 1980, 59, 479.

Figure 1 Effect of varying the dipolar dephasing time (t_1) on the logarithm of the signal intensity, (I_{Ali}) from aliphatic carbon in Condor carbonaceous kerogen. The line is an exponential function fitted to the data at $t_1 > 40$ μs.
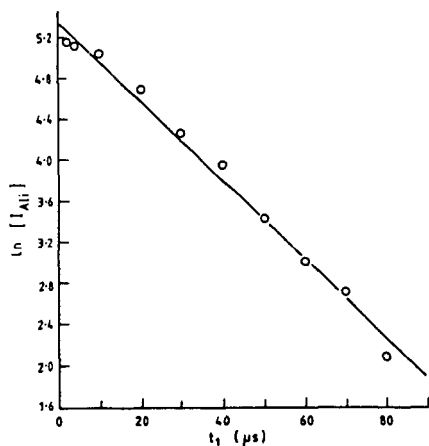
Figure 2 Effect of varying the dipolar dephasing time (t_1) on the logarithm of the signal intensity (I_{Ali}) from aliphatic carbon in Rundle kerogen.
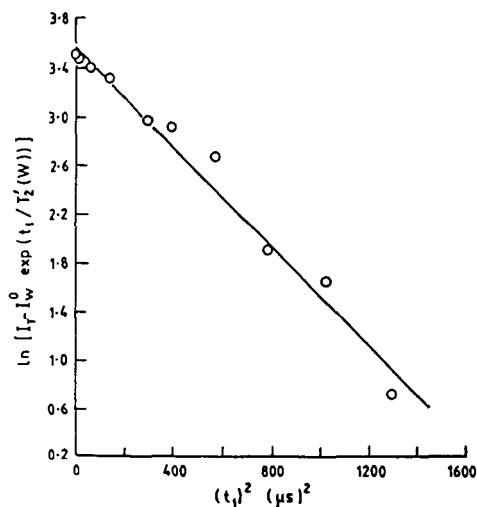

Figure 3 Plot of the square of the dipolar dephasing time (for $t_1 < 40$ μs) against the logarithm of signal intensity from strongly coupled aliphatic carbon (CH_2,CH) in Condor carbonaceous kerogen.
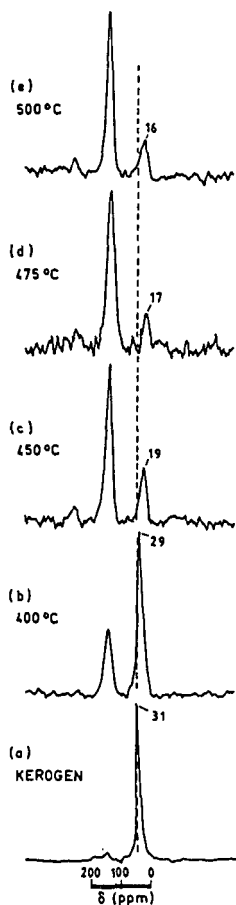

Figure 4 CP/MAS ^{13}C n.m.r. spectra of Rundle kerogen and residues. a) kerogen; residue prepared at: b) 400°C, c) 450°C, d) 475°C, e) 500°C. Note that there is a decrease in chemical shift of the aliphatic resonance with increase in pyrolysis temperature.
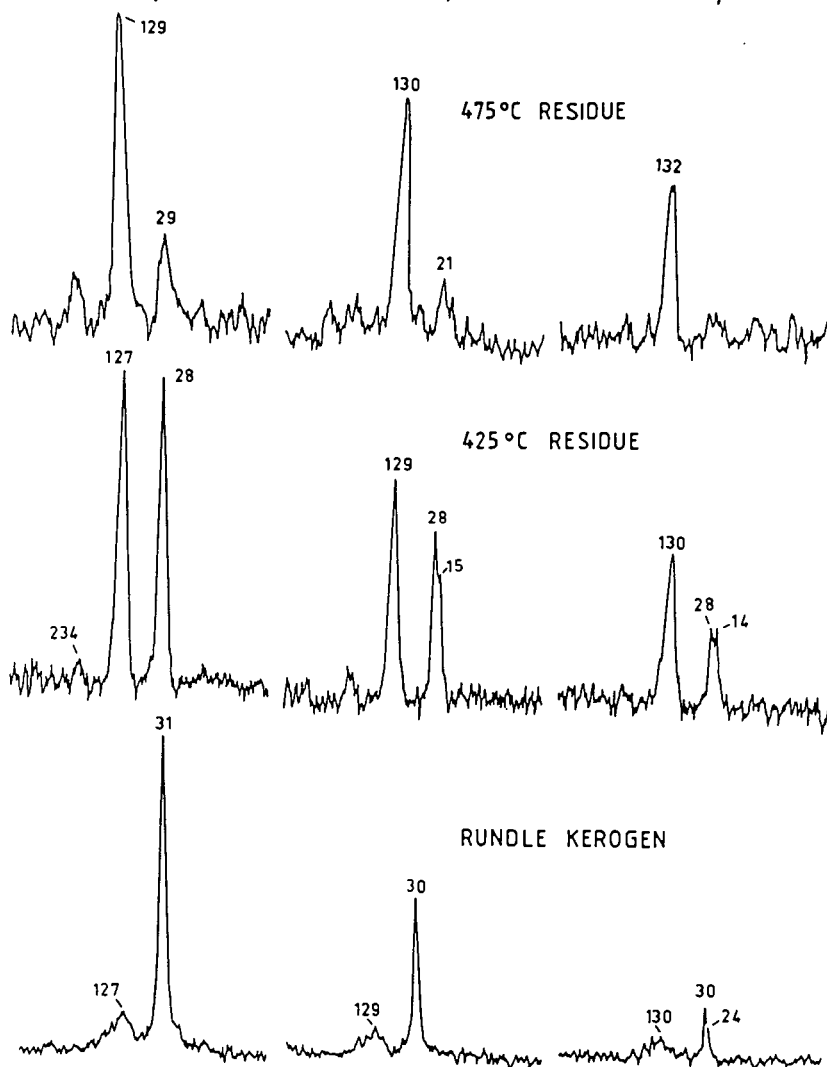
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Figure 5 Dipolar dephased spectra of Rundle shale and residues prepared by pyrolysis at 425 and 475°C respectively. The dipolar dephasing times were a) 2 μs, b) 30 μs, c) 60 μs.